FINAL PUBLISHABLE REPORT

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RMG: -		

TABLE OF CONTENTS

1 Overview

The EU Energy Strategy for transport and the dedicated European policy objectives encourage the wide use of hydrogen for the transport sector. The fast evolution of the hydrogen sector pushes to reconsider the international normative documents. The project addressed the standardisation needs in the hydrogen-energy sector by supplementing and feeding four ISO standards in development or in revision through metrology research studies: ISO 14687, ISO 16111, ISO 19880-8 and ISO 21087. This project provided to the standardisation bodies the guarantee of validated techniques and traceable analysis measurements at the highest accuracy levels.

2 Need

The use of hydrogen is a promising solution to solve the conflict between the growing need for energy, the depletion of fossil fuels, the greenhouse effect and the climate change challenge. The ongoing technical and scientific developments in hydrogen quality control, hydrogen transportation application, distribution, production and storage of hydrogen require constant reassessment of the regulatory documents.

The European Directive on the deployment of alternative fuels infrastructure 2014/94/EU stated that the hydrogen purity dispensed at hydrogen refuelling stations should comply with the technical specifications included in ISO 14687-2. The rapid progress of the fuel cell electric vehicles required revising this standard towards less constraining detection limits and simultaneously ensuring a low impact risk of impurities on fuel cells (ISO 19880-8). Validated analytical techniques, used to measure each impurity in hydrogen according to these specifications, needed in turn to be standardised in a new standard including validated protocols. There was a need to comply both with accurate analytical measurements at low levels of concentration respecting ISO 14687 specifications with validated techniques. In addition, for cost purpose, the number of required analyses had to be reduced using a multi-component analyser.

The normative framework related to ISO 16111 for hydrogen absorbed in reversible metal hydride was improved in the Working Group 25 within ISO/TC 197 by broadening the scope of the former version of the standard published in 2008 to larger hydrogen volumes through traceable methods for the measurement of the amount of hydrogen absorbed in the metal hydrides. There was a need to provide accurate measurements by validated methods (mass methods or flowmeters). One objective of the project was to contribute to the improvement of the hydrogen mass measurement method and its validation.

3 Objectives

This project outputs aimed at feeding the revisions and development of four ISO standards dealing with hydrogen characteristics used for transportation and storage.

The specific technical objectives of the project were to:

1. Develop hydrogen quality specifications for fuel cell vehicles, including tolerance levels for impurities in hydrogen and limits for the degradation of fuel cell performance as per ISO 14687-2 ‘Hydrogen fuel - Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles 2012’. This included recommendations on maximum concentration of individual compounds based on the new fuel cell degradation studies and on the probability of presence.
2. Propose optimised analytical protocols (including fit-for-purpose analytical methods) and assess an analyser that would enable the implementation of ISO 14687-2. The multicomponent analyser should have optimised sampling analysis and met the required detection limits as per business plans ISO/TC 197 “Hydrogen technologies” 2005-11-07 and CEN/TC 268 “Cryogenic vessels and specific hydrogen technologies applications” 2014-04-04.
3. Develop and validate traceable methods for measuring the hydrogen mass absorbed in storage tanks (hydrides AB, AB2 and AB5), with reference to ISO 16111 “Developing transportable gas storage devices - Hydrogen absorbed in reversible metal hydride”.
4. Contribute to the standards development work of key European and International Standards Developing Organisations ensuring that the outputs of the project were aligned with their needs, communicated

quickly to those developing the standards and to those who use them, and in a form that could be incorporated into the standards at the earliest opportunity.

4 Results

4.1 Objective 1: develop hydrogen quality specifications for fuel cell vehicles

The first objective of the project aimed at the development of hydrogen quality specifications for fuel cell vehicles, including tolerance levels for impurities in hydrogen and limits for the degradation of fuel cell performance for a revision of the ISO standard 14687-2 '*Hydrogen fuel - Product specification – Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles 2012'*. Further, several recommendations were made on maximum concentration of individual compounds based on new fuel cell degradation studies carried out by CEA and on the probability of presence determined by the hydrogen production process.

A. Work carried out

The presence of various contaminants in hydrogen for automotive polymer electrolyte membrane fuel cells (PEMFCs) can cause detrimental fuel cell (FC) system damage. Ammonia and halogen-containing impurities are of particular importance due to their prevalence and complex impact on FC performance. The effect of NH_3 and Cl-based molecules on the electrochemical performance of PEMFCs has been tested by determining the impact of 2 ppm of NH_3, 0.2 ppm of HCl and 0.2 ppm of 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane ($C_4Cl_4F_6$) on a FC performance under stationary and dynamic test protocol of overall ~900 h duration. Further, a comparison with the state-of-the-art data was made.

A risk assessment was made for the probability of occurrence of ISO 14687-2 gaseous contaminants (13 in total) in hydrogen. This assessment focussed on the following H_2 production processes: steam methane reforming and electrolysis (water and chlor-alkali) production processes model. The risk assessment approach proposed in ISO 19880-8 including the existing barriers has been investigated within the framework of the Hydrogen project. More than twenty samples from different hydrogen production processes (i.e. steam methane reforming with pressure swing adsorption, PEM water electrolyser with temperature swing adsorption) were analysed according to ISO 14687-2 requirements. The results were used to validate the probability of occurrence of ISO 14687-2 gaseous contaminants (13 in total) in hydrogen proposed in the project for steam methane reforming (SMR) with pressure swing adsorption(PSA) and PEM water (PEMW) electrolysis with Temperature-Swing Adsorption (TSA).

B. Key outputs & conclusions

The three contaminants (NH_3, HCl and $C_4Cl_4F_6$) all induced reversible and irreversible FC performance losses over a long-term test (between -27 and - 47 μV/h irrecoverable between beginning of test and end of test), which were considerably larger compared to the ones for baseline test in pure H_2 (-10 μV/h). The most harmful effect was observed after FC cell exposure to $C_4Cl_4F_6$. The performance decay for the cells tested with the pollutants was partially recovered via electrochemical characterisation and cell decontamination in neat H_2 applied after each phase of the test. In-situ advanced electrochemical characterisation and ex-situ microscopy study allowed understanding the poisoning process.

Probability of presence was determined for the 13 gaseous contaminants (ISO 14687-2) in hydrogen on 3 production processes: SMR process with PSA, chlor-alkali membrane electrolysis process and water proton exchange membrane electrolysis process with temperature swing adsorption. The rationale behind the probability of contaminant presence according to process knowledge and existing barriers was highlighted. No contaminant was identified as possible or frequent for the three production processes except oxygen (frequent for chlor-alkali membrane process), carbon monoxide(frequent) and nitrogen (possible) for SMR with PSA. The results of the analytical campaign confirmed the absence of contaminants for the hydrogen from production processes SMR with PSA and PEMW electrolyser with TSA. The agreement between the results of the analytical campaign and the probability assessment of presence of contaminants supports the approach of ISO 19880-8. This project can be used as an example to implement ISO 19880-8. Based on it, a hydrogen quality assurance plan following ISO 19880-8 can be devised to support hydrogen providers in monitoring the relevant contaminants.

4.2 Objective 2: optimised analytical protocols and assess an analyser that enables the implementation of ISO 14687-2

In the second objective, optimised analytical protocols were proposed (including fit-for-purpose analytical methods) and analysers that enable the implementation of ISO 14687-2 were assessed. Special attention was paid to multi-component analysers as they had the potential to reduce the number of analyses and consequently maybe also reduce cost. Further, optimised sampling analysis and the ability to meet the required detection limits was considered.

A. Work carried out

Project partners contacted several manufacturers of analytical equipment to discuss the capabilities of their instruments for H_2 purity analysis. In addition, some in-house developed instruments and methods were included in the analyser's comparison. The activity on multi-component analysers focused on spectroscopic instruments, although some other methods (e.g. gas chromatographs or mass spectrometer-based instruments) also offer such capabilities.

B. Key outputs & conclusions

The NMI's VSl, NPL, RISE and CEM developed analytical fit-for-purpose methods for some gaseous impurities listed in ISO 14687-2. These include a gas chromatographic method for hydrocarbons (RISE), spectroscopic methods for ammonia, formic acid, formaldehyde and hydrogen chloride (VSL), and cry-GC-SCD methods for sulphurs (NPL).

As an example, Figure 1 shows a measurement of low amount fractions of hydrogen chloride (HCl) using the spectroscopic method developed at VSL. The sensitivity of the developed method is enough to comply with limit set in ISO 14687-2 for total halogenates (specification value 50 nmol/mol).

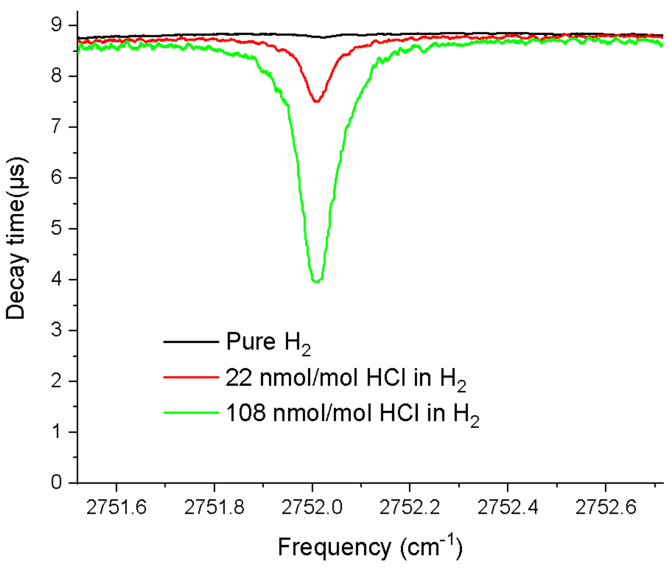

Figure 1 Measurement of low amount fractions of HCl in H_2 using cavity ring down spectroscopy. Also shown is a measurement of pure hydrogen. The HCl mixtures were generated by diluting a HCl in N_2 standard with pure H_2.

Using multi-component analysers has been found to be a promising way to reduce the number of analyses needed to assess the quality of hydrogen according to ISO14687-2 mostly due to the flexibility with these instruments. These instruments are often designed based on the client´s requirements; one of which is the selection of compounds to be analysed. In this way, every lab is free to select the compounds that cannot yet be analysed using other instruments available at the laboratory. However, there is currently a lack of a proper validation of these instruments. It is therefore important that external laboratories like National Metrological institutes perform a complete validation of the instruments using well established procedures and certified reference materials. Several documents are available to guide a laboratory through a method validation including the Eurachem guide “The Fitness for purpose of analytical methods”. ISO TC158 is working on a new standard ISO/DIS 21087 proposing a detailed approach for the validation process. The study performed in the Hydrogen project demonstrates that there is a need of standardisation and method validation for the multi-component analysers commercially available. Reported performance criteria of commercial multi-components analysers are indeed not easily available which makes difficult the selection of analysers for commercial analytical laboratories.

Another conclusion of the work carried out for the objective 2 is that many other analytical methods that can meet the thresholds set in ISO14687-2 still require proper validation. Only after a proper validation it can be decided whether these methods are fit for purpose, using the criteria established in ISO 21087.

A report on the multi-component analysers can be found at http://projects.lne.eu/jrp-hydrogen/download/2348/

4.3 Objective 3: develop and validate traceable methods for measuring the hydrogen mass absorbed in storage tanks

The third objective focussed on the development and validation of traceable methods for measuring the hydrogen mass absorbed in storage tanks (using hydrides AB, AB2 and AB5). Hydrogen storage by reversible hydride metal is more and more used in various storage systems. However, this storage method does not provide one-to-one relationship between absorbed mass of hydrogen, pressure and temperature. The knowledge of observed physical variables like pressure and temperature is not enough to assess the residual hydrogen contained in the tank. The work carried out here was done with reference to the ISO standard 16111 “*Developing transportable gas storage devices - Hydrogen absorbed in reversible metal hydride*”. This ISO standard is devoted to this type of tank. ISO/TC 197/WG 25 is working on a revision of this standard. Particularly, issues arise as the standard states that a hydrogen cycling test must be performed during qualification test and that the tank shall be cycled when charged with hydrogen, from not more than 5 % of rated capacity to not less than 95 % of rated capacity. ISO 16111 does not currently recommend the use of any specific measurement technique or method with respect to the cycle test. The work carried out in the Hydrogen project was done with the objective to make proposals for accurate measurement methods of the hydrogen residues with uncertainties associated.

While measuring the hydrogen mass absorbed in storage tanks might seem trivial it turns out that different methods (mass based versus flow rate based) often give different outcomes.

A. Work carried out

Project partner MAHYTEC has provided tanks with 2 types of hydrides to two other project partners FHA and CEA-Liten. The tanks contain 100 g hydride (in which about 1.5 g of H_2 can be absorbed) and have a total weight of 650 - 700 g. The tanks were supplied with a valve and a self-sealing nozzle. There are mainly two methods for the determination of the volume stored in the tanks; mass measurement (weighing method) and flow measurements method. The focus here was on the second, the flow measurement method.
Each partner involved was free to develop and use its own measurement method. The goal was to compare the measurement results (accuracy, reproducibility) with different methods for the same tank. The main difficulty was the very high difference between the mass of the tank and the small mass of the stored hydrogen. Two methods for flow measurements were investigated. FHA designed a test rig based on a combination of mass flow meters and needle valves and CEA-Liten built-up a test rig primary consisting of a single mass flow controller.

The partners carried out many loadings and unloading of the tanks monitoring flow rates and pressure in the tank. A typical example is shown in Figure 2.

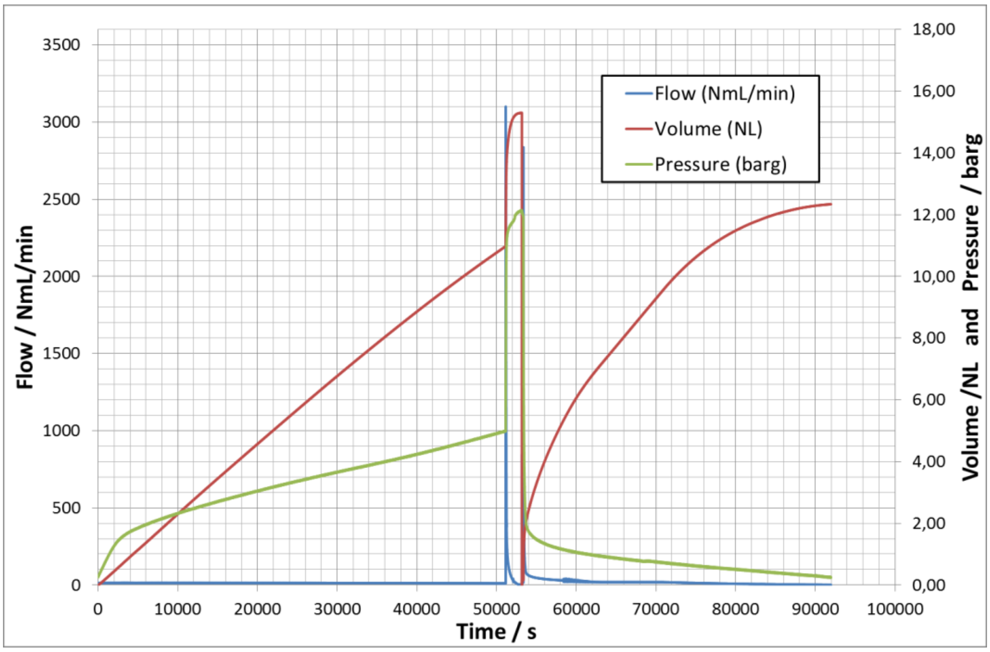

Figure 2 Typical example of filling and emptying of tank with hydrogen.

B. Key outputs & conclusions

Concerning the design with needle valves, this construction of the test bench allowed constant flow rates during loading and unloading, but the mass flow meter worked at two different pressures: a quite constant pressure during loading, during unloading the pressure is fixed by the outlet pressure (atmospheric pressure in our case). Adding needle valves, restrains the pressure range attainable because of the pressure loss they introduce in the circuit. The most visible consequence will be that mass flow rate for the end of each loading or unloading period will be reduced, and some of the capacity measure of the tank will be restrained by earlier cut-off of the mass flowmeter measure.

Concerning the design with a mass flow controller, this design is a bit simpler than with needle valves. It permits to control the flow rate that does not vary too much during the measure, but the pressure of use of the mass flow meter is not the same when loading and unloading.

Both solutions require the mass flowmeter to work under different pressure for loading and unloading phases. Around source pressure for the loading, and around the outlet pressure for the unloading phase. Thus, both solutions require a calibration of the mass flowmeter at two pressures.

The idea of using needle valves was guided by the choice of avoiding using a mass flow controller, but this solution includes a gas circuit which is a bit more complicated with more components. Moreover, it suffers from a pronounced "saturation" effect, which makes the mass flowmeter to work in a saturated state and is expected to generate an uncontrolled measure deviation. Overall it can be concluded that measuring the tank capacity with thermal mass flowmeters seems to be the best solution, yet this method has some subtilties as a large range of flow rates and pressures are involved. Furthermore, thermal mass flowmeters, even though frequently used for measuring tank capacity, have modest accuracy.

5 Impact

Continuous activities have been undertaken to support the uptake and use of the project’s outputs to the stakeholder hydrogen community (industrial and regulatory organisations). The consortium has given a substantial number of technical and general presentations of the project’s outputs at international events.

Impact on industrial and other user communities

The industrial and user communities of hydrogen were the targeted beneficiaries of the project outputs. The uptake of the expected knowledge and methods from the project had a direct effect on the hydrogen industrial community: producers, consumers, distributors and manufacturers of analytical gas analysers and storage tanks. Follow-on collaborations with companies or laboratories not involved in the project as Shell, ITM power, SINTEF, LINDE and CNH2 enabled the achievement of objectives in terms of impurities measurements. AP2E Company, a collaborator of the project, promoted a project output for commercial use towards prospective customers. Moreover, AP2E organised a round-table debate at the Industrial Analysis Exhibition in February 2018 with project's partners questioning the adequate gas analysis methods to control the purity of the hydrogen in order to support the market development of fuel cells. Two articles were published in professional journals in 2018 promoting the project dealing with hydrogen quality. More than four publications have been published in *Gasworld*, *Mesures, Hydrogen Platform,* on the *hydrogen purity* Wikipedia page and on a partner's general website.

Industrial stakeholders as fuel cells manufacturers, gas analyser manufacturer or hydrogen producers reiterated their interest to be member of the stakeholder advisory board and to be informed of the expected outputs of the project. A wide variety of international industries, automotive and spatial industries, hydrogen producers, hydrogen storage and distribution companies, research centres, gas analysers manufacturers and investment banks attended the international workshop of the *Hydrogen* project held at the Air Liquide R&D Centre "Campus Innovation Paris". The hydrogen project was identified at the new European Metrology Network on Energy Gases launched in 2019.

Impact on the metrology and scientific communities

This project was the first metrology European project related to hydrogen within the EMPIR Programme. The wider impact was that metrology for hydrogen purposes in industry, standardisation or other user communities became the guarantee for validated techniques and traceable measurements in any hydrogen topic.

Results have been presented at 23 international conferences and six papers have been published or submitted to dedicated scientific journals: one paper has been published in *Measurement Science and Technology* following the International Congress of Metrology 2017, another one was an Open-Access publication in the *International Journal of Hydrogen Energy* (2018), two papers were included in proceedings books of conferences (Iberconappice and ISFFM) and two open-access papers have been submitted respectively to the *Journal of Power Sources* and *International Journal of Hydrogen Energy*.

The website of the project was regularly updated at http://projects.lne.eu/jrp-hydrogen/ with news items or information regarding events or conference attendance.

Impact on relevant standards

Through the dissemination of the project outputs at the CEN and ISO level, answering cross-cutting issues through metrology studies provided new knowledge for the improvement of standards. The exploitation of results directly impacted the standardisation works following the close interactions between partners of the project and their commitment in the working groups of ISO/TC 197. Outputs of the project impacted the standardisation works in the relevant working groups of the International and European regulatory bodies: at ISO/TC 197 / WG 28 for hydrogen quality control, ISO/TC 197/WG 27 for hydrogen fuel quality and ISO/TC 197 – ISO/TC 158 / JWG7 for hydrogen fuel analytical methods. All deliverables of the project were sent to decision makers at working groups of ISO/TC 197. In addition, regular information and work-in-progress have been relayed at national mirror ISO/TC 197 committee meetings.

Longer-term economic, social and environmental impacts

Zero-emission vehicles use as fuel cells electric vehicles powered with hydrogen reduces the pollution levels in urban areas. In addition, if this hydrogen is produced from renewable energy sources, it is the energy solution to mitigate the impacts of global climate change and the alternative renewable energy to fossil fuels. The project results with a global aim to enhance hydrogen use for mobility and storage will, in its entirety, have an environmental impact on hydrogen vehicles use through the consideration at standardisation ISO/TC 197.

It leads also to a potential effect on developing countries' populations that are encouraged for many years to support International and European standards to promote hydrogen use as an energy fuel and to decrease their dependency of fossil fuels.

The scientific result related to the impact tests of three key impurities on fuel cell performance led to suggest relaxing ammonia specification for further consideration at ISO/TC 197/ WG 27. If considered for future revision of ISO 14687, this will have a wider economically impact both the fuel cells manufacturers and hydrogen producers and consequently the gas analysers manufacturers to adopt less stringent but also validated technique for ammonia.

Moreover, achieving durable cost reduction of hydrogen technologies associated with its production, transport and utilisation is a matter somehow of defining hydrogen characteristics to ensure access to a product of quality. The ability to easily control hydrogen purity was an important issue not only for fuel cells manufacturers that ensured the reliability and lifespan of their products by the ISO 19880-8 application, but also for users who have now the guarantee of the performance of fuel cells. By developing the risk assessment matrix of impurities taking into consideration the probability of presence of hydrogen impurities and their impact in terms of toxicity, the reliability and lifespan of fuel cells will be guaranteed through the ISO 19880-8 application.

In parallel, the project aimed at assessing the status of the analytical methods available in the market for hydrogen impurities accurate measurements in terms of performance characteristics and validation data, at assessing multi-component analysers (FTIR, OFCEAS, CRDS, BLT) through discussion with providers, end-users and literature study to reduce the number of analyses totally required and at developing and validating three speciation methods for S-compounds, halogenated (HCl) and hydrocarbons. The outputs linked to this last objective have been transferred to be a documentary support at ISO/TC 197 - ISO/TC 158 JWG 7 (hydrogen fuel analytical methods) to ensure hydrogen quality for fuel cell applications for road vehicles. He document will help gas analysers' manufacturers to propose fit-for purpose validated analytical methods enabling the implementation of ISO 14687 based on their clients' requirements for characteristics performances (selectivity, trueness, precision and working range), costs and possibly other specific requirements as response time, volume the gas needed or the possibility to work with different gas matrices.

At the same time, hydrogen use as a safe energy must be accepted by the public and education is needed to overcome the feeling of fear that remains mainly when thinking of any hydrogen application. The international workshop held at Campus Innovation Paris (Air Liquide R&D Centre) where training courses have been given to people coming from various hydrogen interests bases. It deeply contributed to the social acceptance of hydrogen as broadly use energy vector. Safe storage of hydrogen in metal hydrides and newest recommendations released within the project is one of the ways to change mindsets.

6 List of publications

- Probability of occurrence of ISO 14687-2 impurities in hydrogen:principles and examples from steam methane reforming and electrolysis(water and chlor-alkali) production processes model,T. Bacquart, A. Murugan, M. Carré, B. Gozlan, F. Auprêtre, F. Haloua, T.A.Aarhaug, *International Journal of Hydrogen Energy*, Vol. 43 (2018) pp. 11872-11883, https://doi.org/10.1016/j.ijhydene.2018.03.084

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